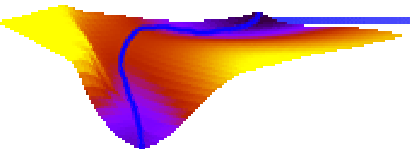
A Chemist view on Reaction Path

P. Fleurat-Lessard

Laboratoire de Chimie

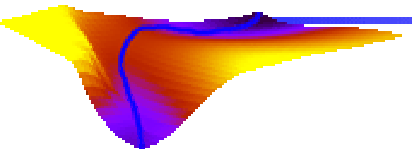
Ecole Normale Supérieure de Lyon

Outline



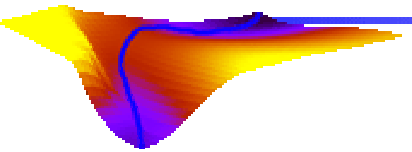
- Why is the chemist view special ?
- Different sets of coordinates
- Applications
- Conclusions

Main concern of the chemist



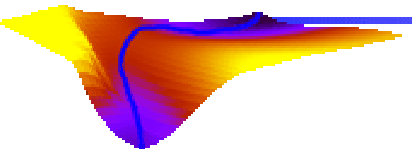
- Bond breaking and forming
  - Quantum approach is needed
  - Cost a lot !
    - Size : 100 QM, 50000 QM/MM
    - Time scale : 10 ps
- Environment is important
  - Protein, solvent
  - Temperature

Textbook example: HCN

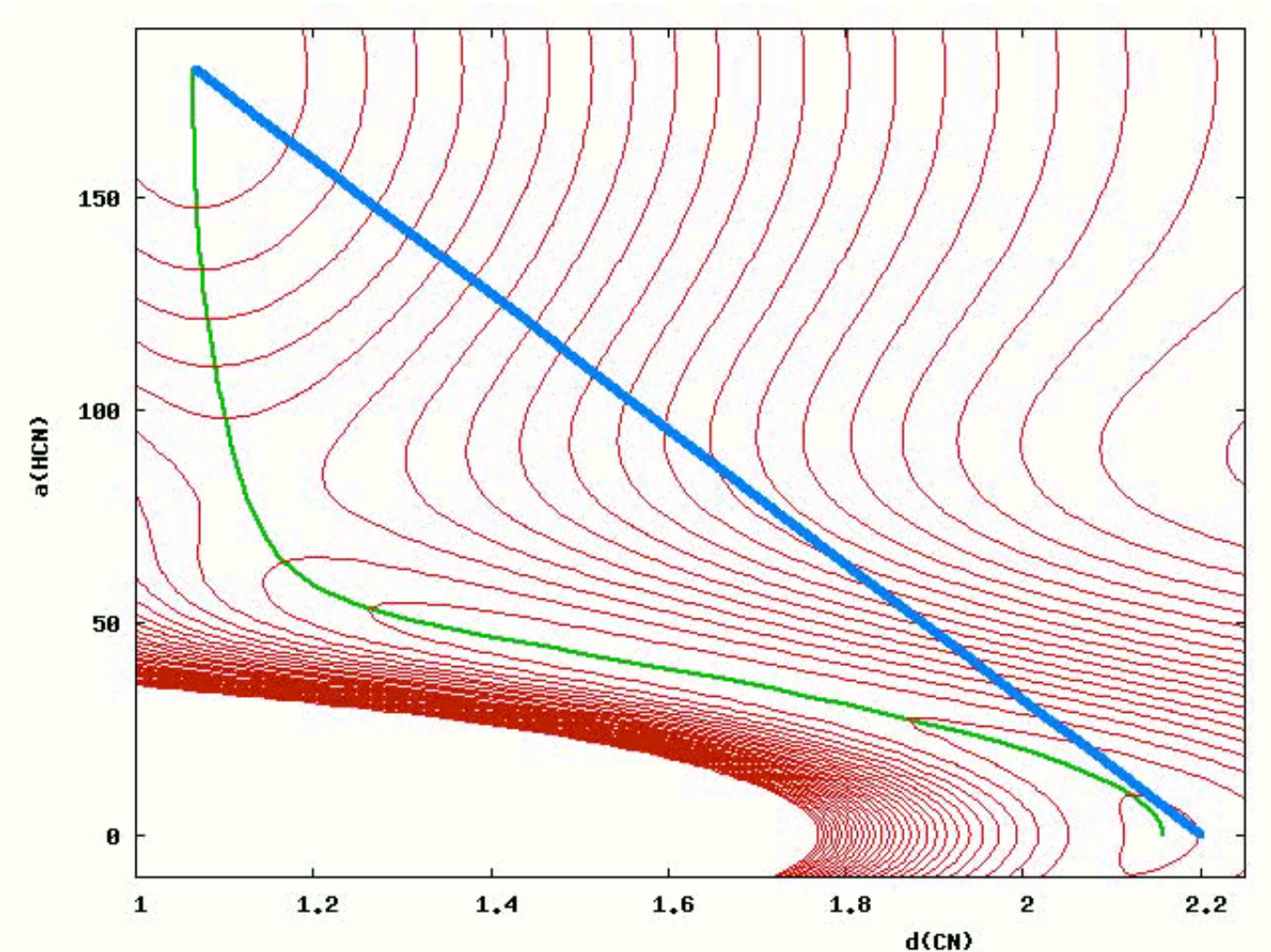


- HCN $\rightarrow$ CNH
  - Reactants and products are known
  - Generate an initial Path connecting the two
  - Optimize it

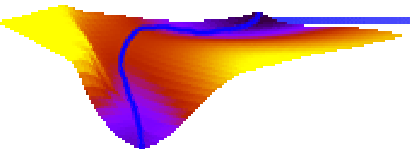
Textbook example: HCN



- HCN $\rightarrow$ CNH
- Result:



But... description is discrete



- How to choose the points ?
  - Equidistant, constant density...
- How to ensure good sampling of the path ?
  - Nudge Elastic Band:
    - Spring between 2 points

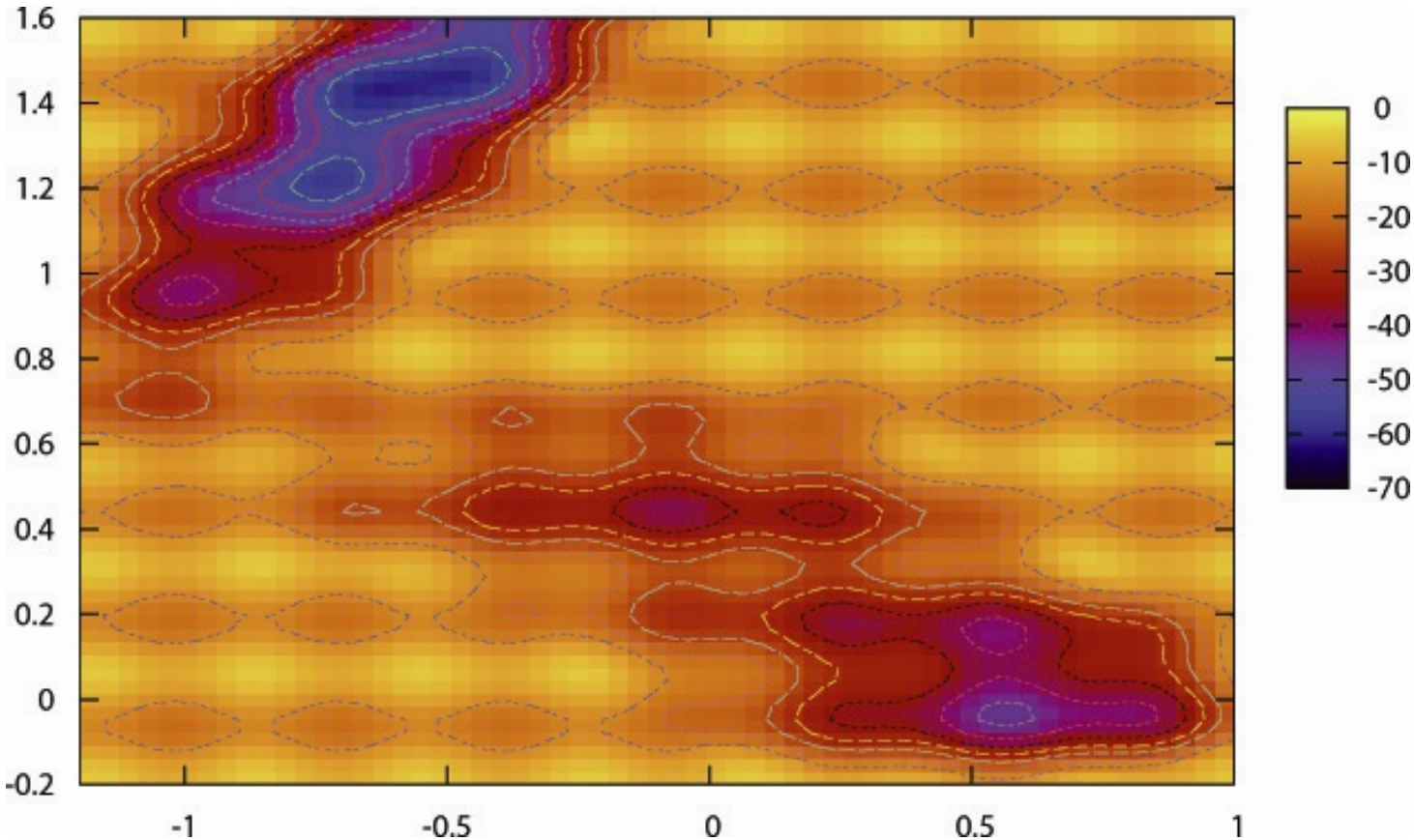
G. Mills, H. Jónsson PRL **1994**, 72, 1124

  - String method:
    - Reparameterization

W. E, W. Ren, E. Vanden-Eijnden PRB **2002**, 66, 052301

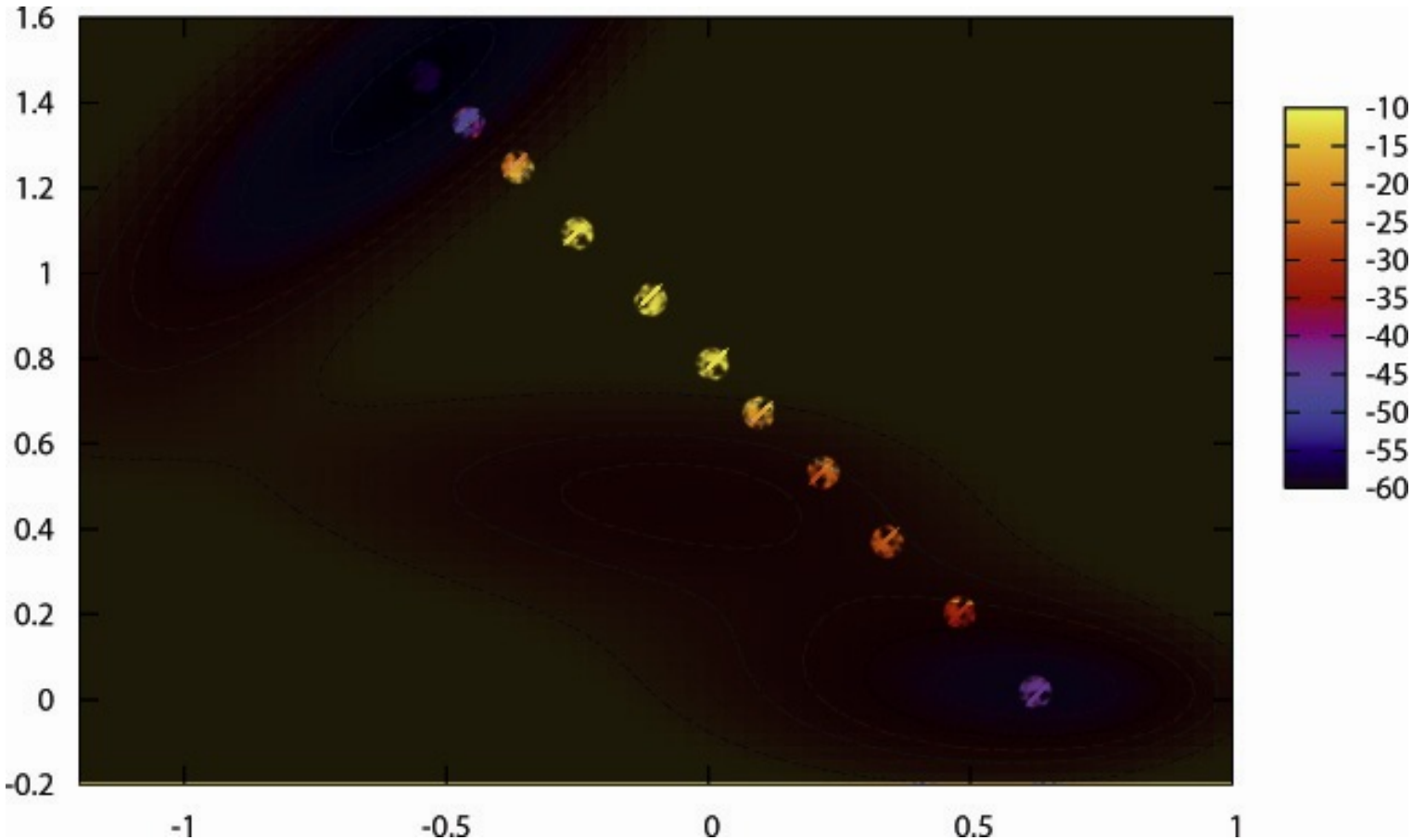
But...

- Realistic Potential Energy Surface is much more complicated:

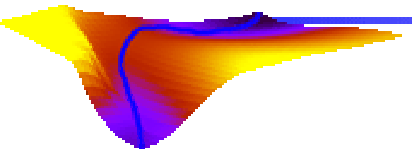


But...

- PES is unkown: we are in the dark



It can get worse...

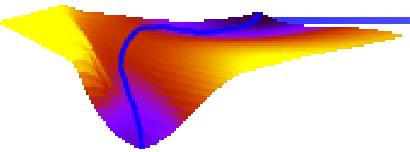


- Actual experiments:
  - Constant T, P: needs MD or MC
  - Environment: lots of objects (atoms, coarse grain...)

  $\Rightarrow$ Cannot afford high dimensionality for Reaction Coordinate
    - Usually 2 or 3

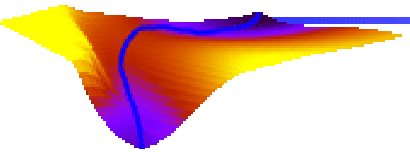
- We **really** need:
  - A good initial path: rough idea of the RCs
  - A good optimizer: we cannot afford 1000 iterations

Coordinates systems



- Lots of discussions for geometries
- Mainly two families:
  - Cartesian coordinates
  - Internal coordinates:
    - Z-Matrix
    - Natural Coordinates
    - Redundant coordinates
    - Baker coordinates

Coordinates systems



- Lots of discussions for geometries
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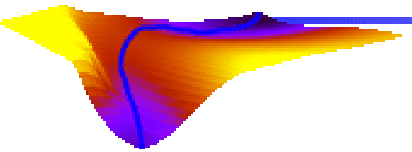
Cartesian coordinates



- Very general
- Easy to compute, store, manipulate

But

- No chemical meaning
- Overall rotation and translation not suppressed

Z-Matrix

- Based on internal coordinates:
  - bond distances, bond angles and dihedrals
- 3N-6 degree of freedom

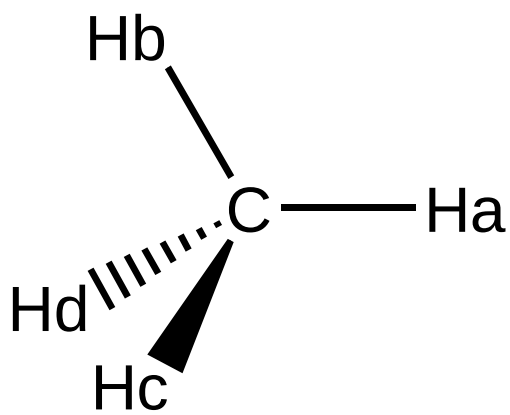
C

H_a C dCH_a

H_b C dCH_b H_a $\alpha H_a CH_b$

H_c C dCH_c H_a $\alpha H_a CH_c$ H_b DH1

H_d C dCH_d H_a $\alpha H_a CH_d$ H_b DH2



Z-Matrix

- Based on internal coordinates:
  - bond distances, bond angles and dihedrals
- 3N-6 degree of freedom

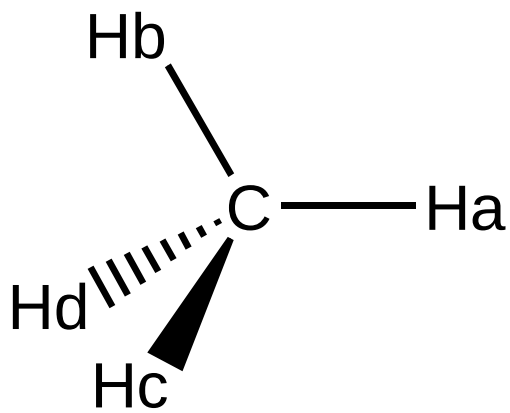
C ← Origin of the frame

H_a C dCH_a ← z axis

H_b C dCH_b H_a $\alpha H_a CH_b$ ← xz plane

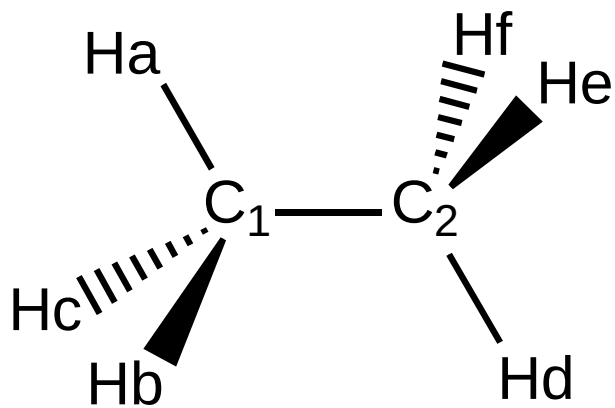
H_c C dCH_c H_a $\alpha H_a CH_c$ H_b DH1

H_d C dCH_d H_a $\alpha H_a CH_d$ H_b DH2



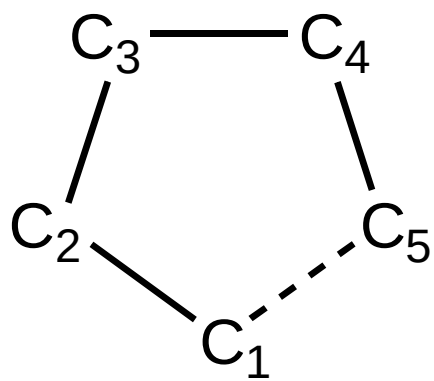
Z-Matrix

- But
  - Non unique
    - How to choose the order of the atoms ?

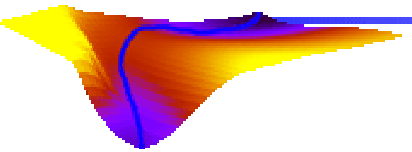


Z-Matrix

- But
  - Non unique
    - How to choose the order of the atoms ?
    - Problem for cycles

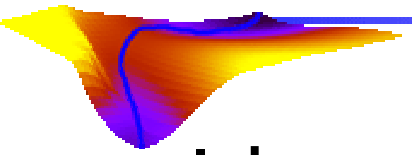


Z-Matrix



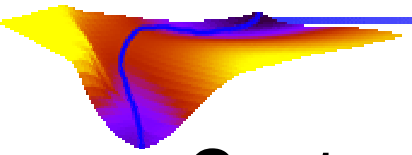
- But
  - Not unique
    - How to choose the order of the atoms ?
    - Problem for cycles
  - Not easy to compute
- Extension: Natural coordinates (Pulay)
  - Use deformations for cycles, combination of distances...
  - Codes of 1000s lines...

Baker coordinates

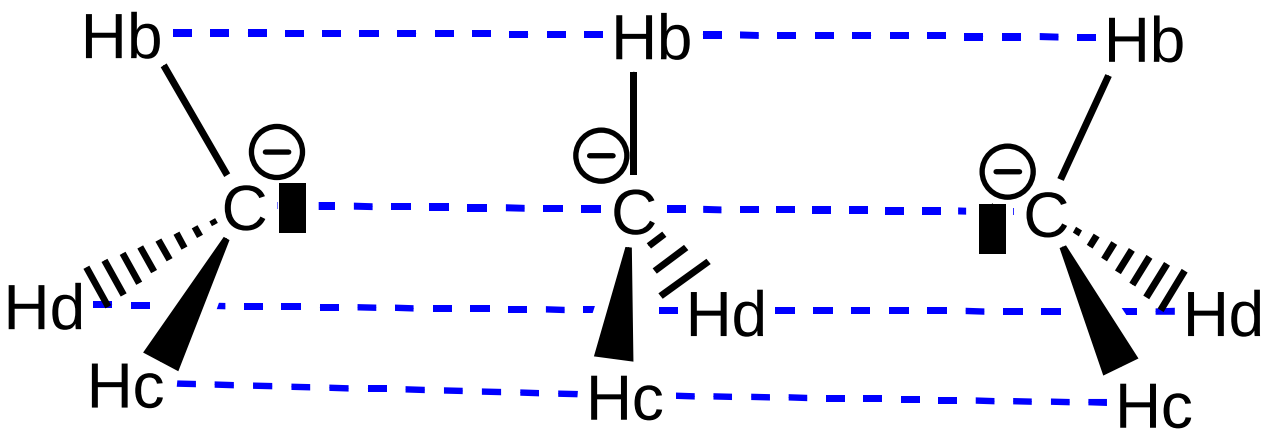


- Idea
  - Generalize Z-Matrix and natural
  - Based on internal coordinates: q_j
  - Keep only the non-redundant combinations
    - Compute Wilson B matrix $B_{ij} = \frac{\partial q_j}{\partial x_i}$
    - Compute G matrix $G = B^t B$ $\quad G_{ij} = \sum_k \frac{\partial q_k}{\partial x_i} \frac{\partial q_k}{\partial x_j}$
    - Diagonalize G
      - 3N-6 non 0 eigenvalues
      - U is the matrix of the eigenvectors

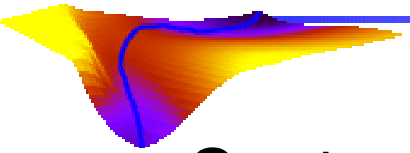
Reaction path coordinates



- Cartesian coordinates
  - Same description for all images
  - But
    - Problem of stretched/compressed bonds



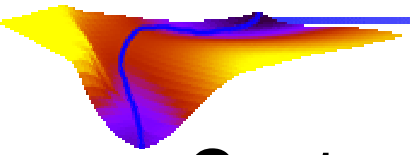
Reaction path coordinates



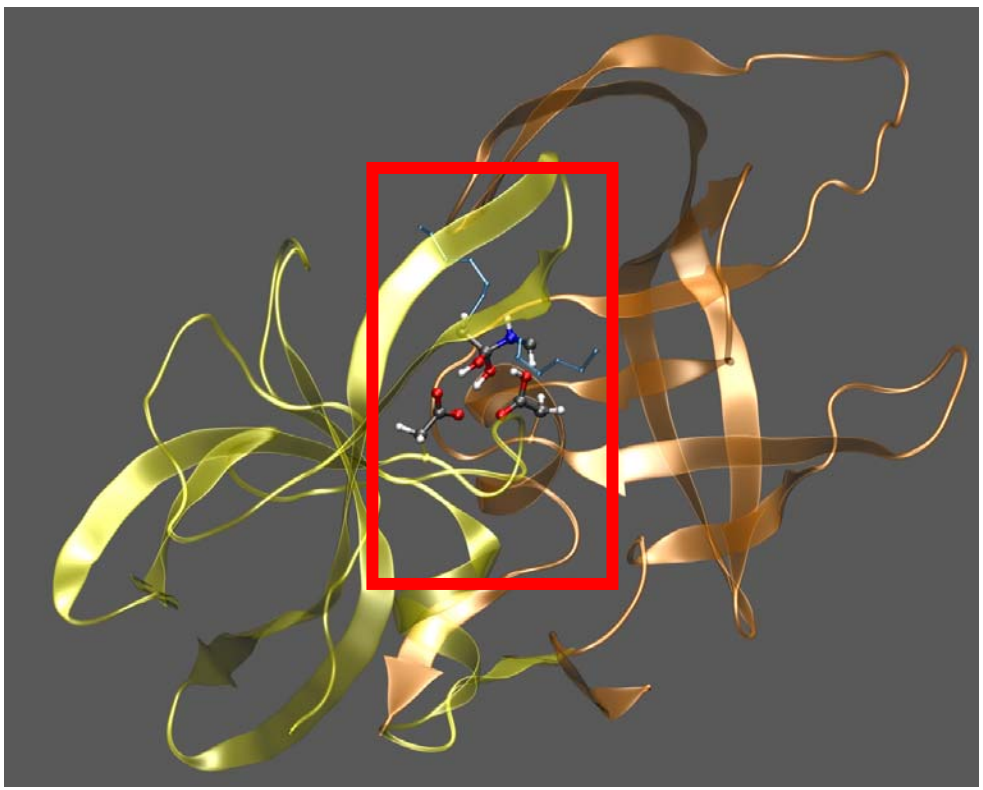
- Cartesian coordinates
  - Same description for all images
  - But
    - Problem of stretched/compressed bonds
    - Stupid path
    - HCN $\rightarrow$ CNH might lead to

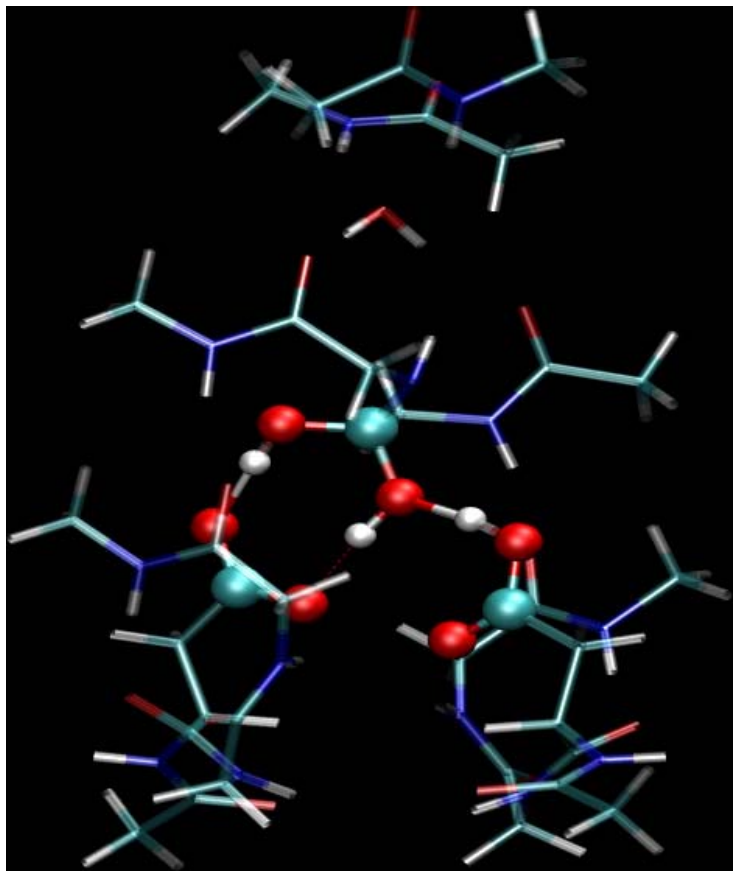
    - Easy to check for HCN...

Reaction path coordinates



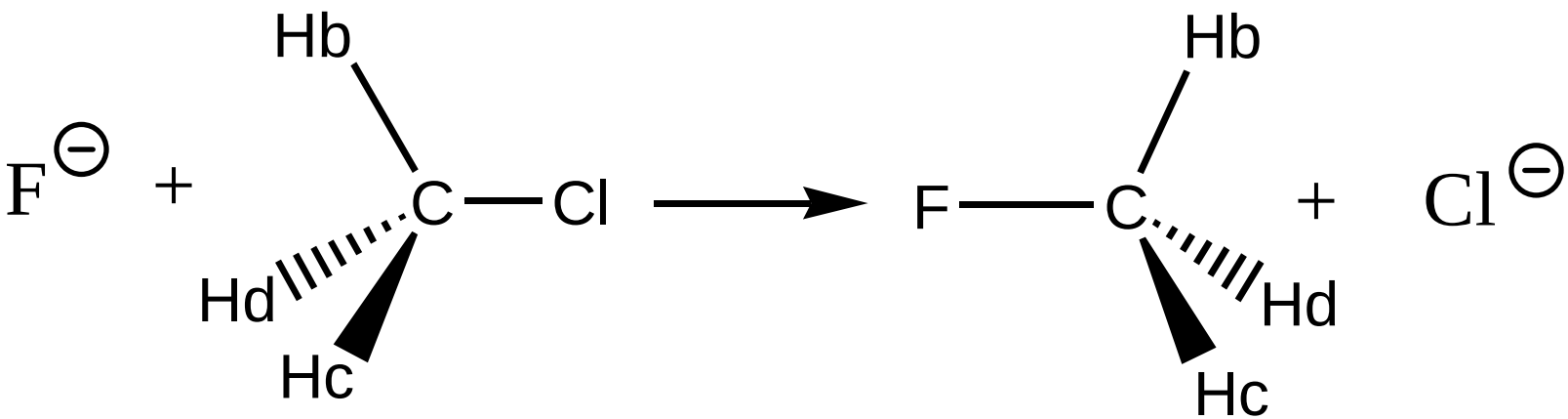
- Cartesian coordinates
  - But not in real life !



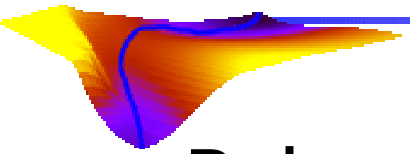


Reaction path coordinates

- Z-Matrix coordinates
  - Less problem of distorted bonds
  - But
    - Which Z-matrix ?

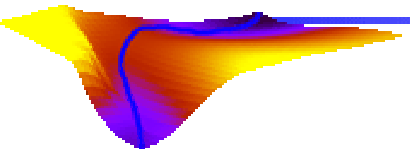


Reaction path coordinates



- Baker coordinates
  - Uses internal from all geometries
    - Less problems of distorted bonds
    - No problem of choosing internal coordinates
  - But
    - Which eigenvectors ?
      - Same U for all geometries
      - Some kind of interpolation
    - Technical problems:
      - Angles becoming close to π
      - Conversion to cartesian...

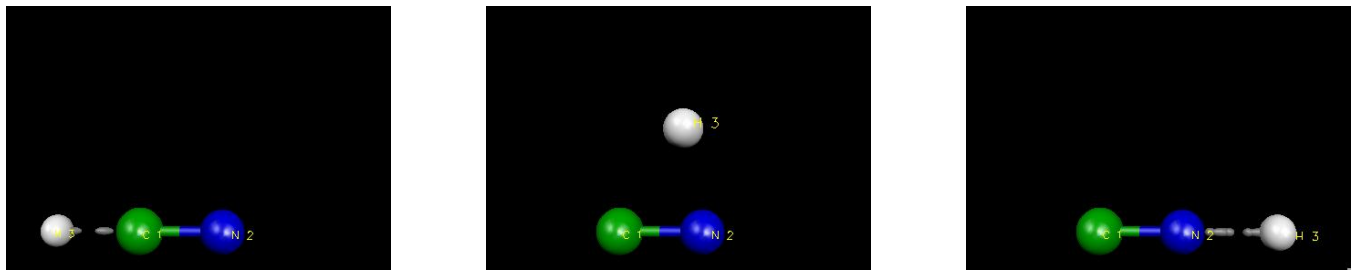
Reaction path coordinates



- Conclusion
  - Baker coordinates disappointing
  - Good description achieved by mixing cartesian and internal

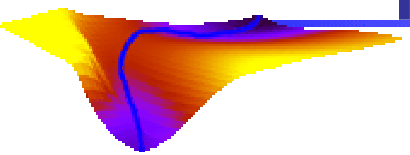
Applications: Back to HCN

- Initial geometries

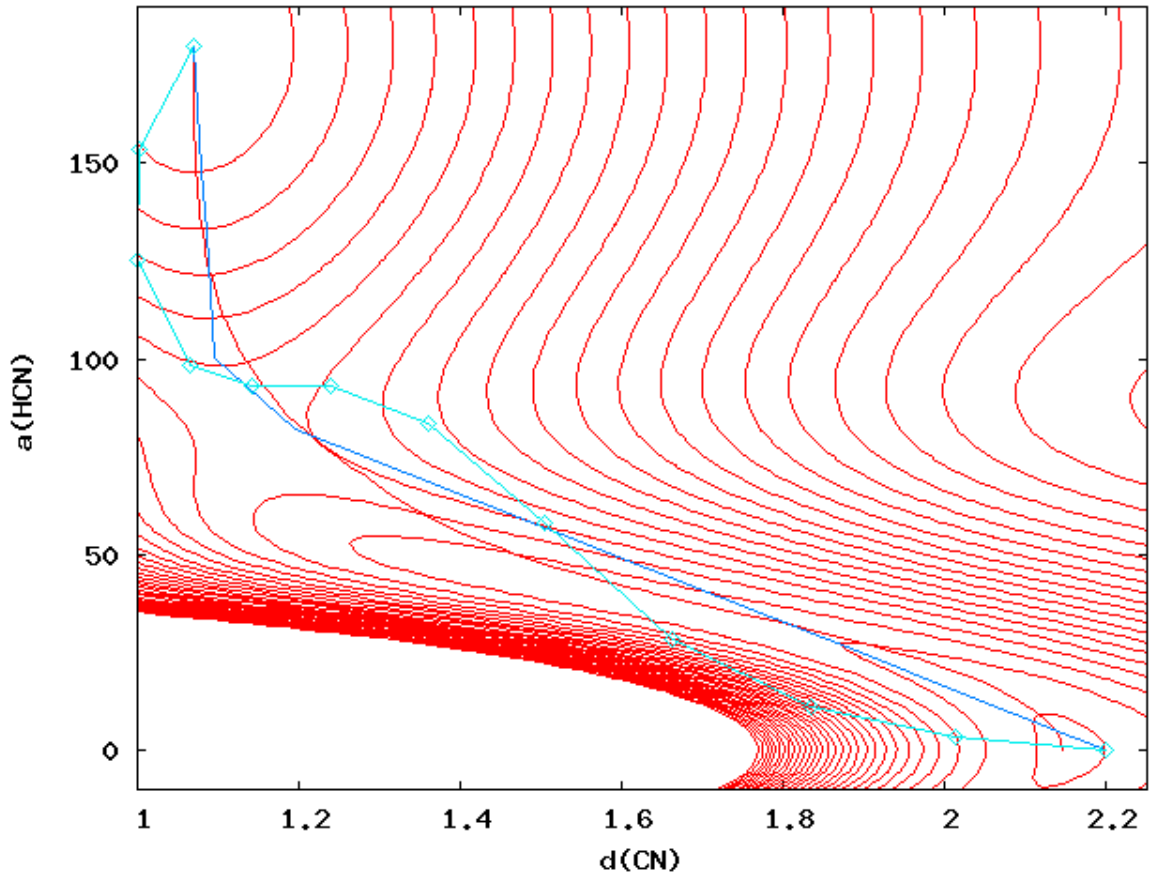


- Computational details
  - Newton-Raphson optimizer with BFGS update
  - Displacement orthogonal to tangents

Applications: Back to HCN

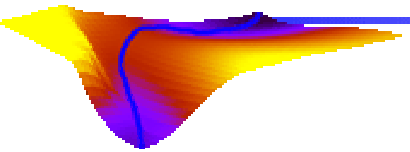


- Initial path

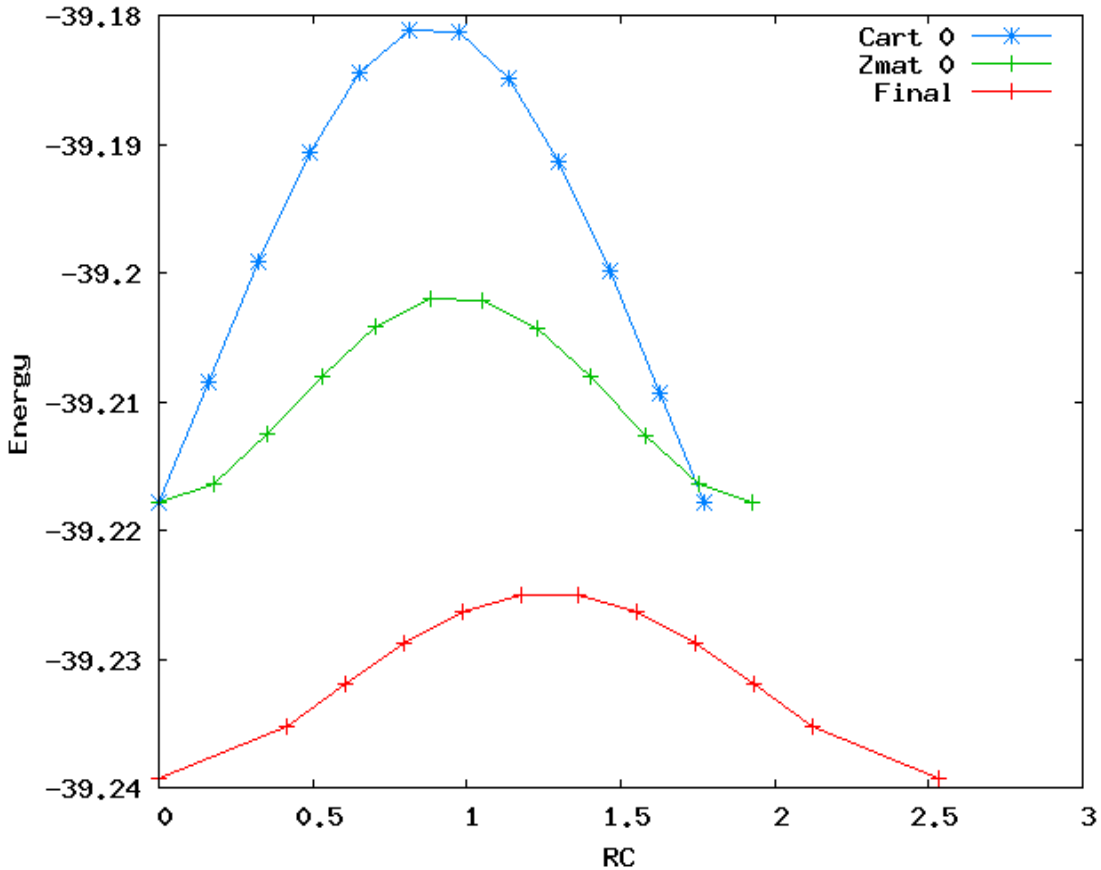


- Convergence
  - Zmat: 8 iterations
  - Cart: 12 iterations

CH_3^- inversion

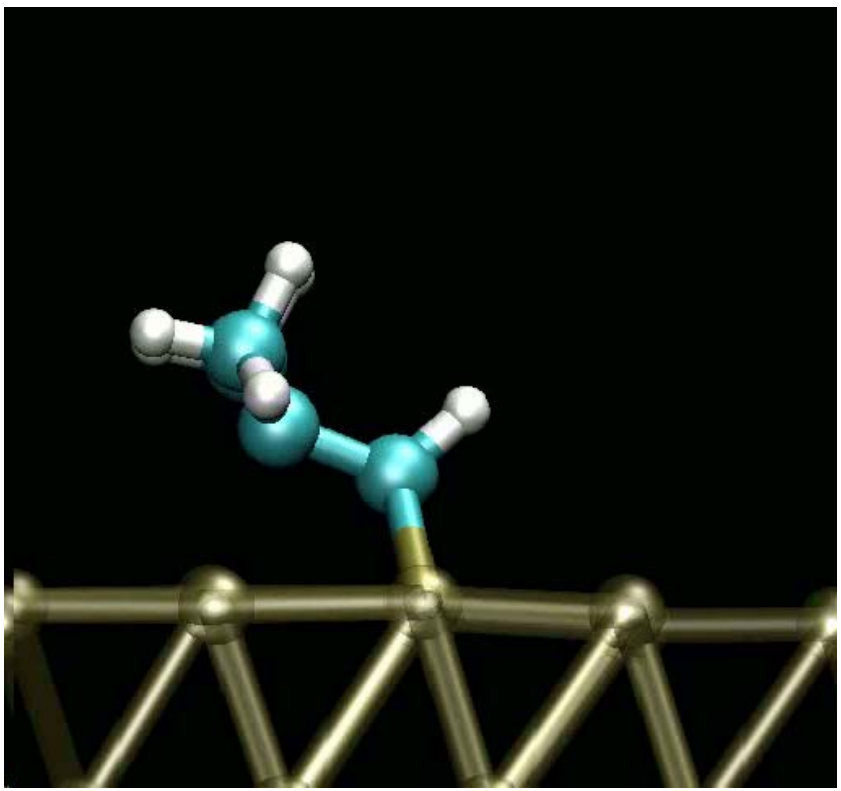


- Walden inversion:
  - Model of SN2 reactions
  - Floppy molecules
  - Cart vs Zmat
    - Initial path better in Zmat
    - Good optimizer
      - cart 8 iterations
      - Zmat 7

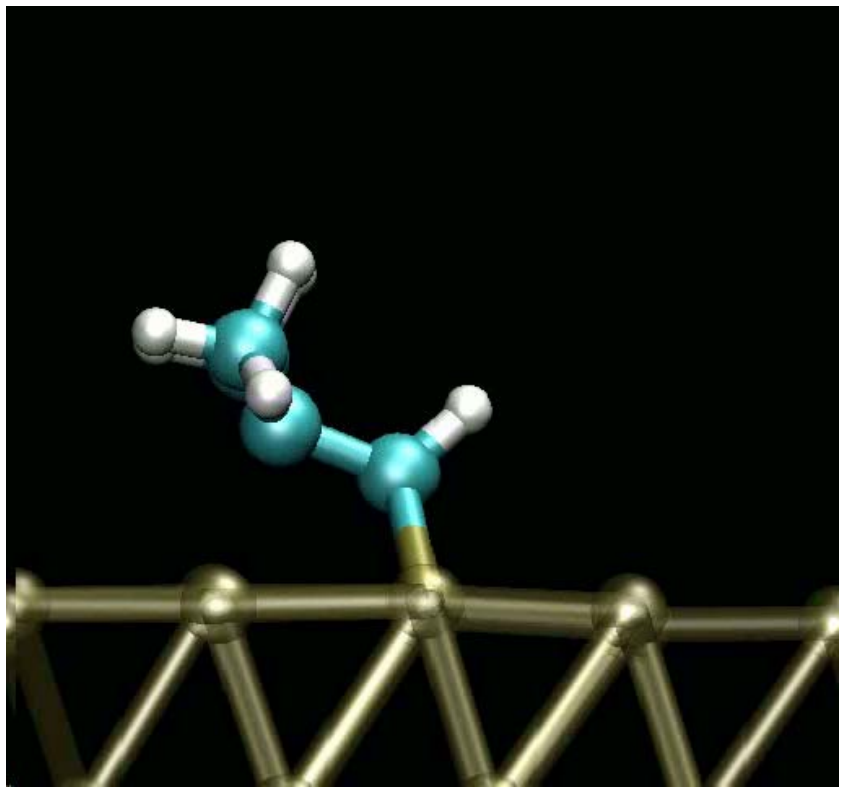


Catalytic hydrogenation on Pt

- Initial paths

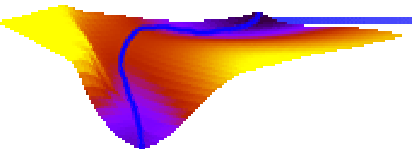


Cart

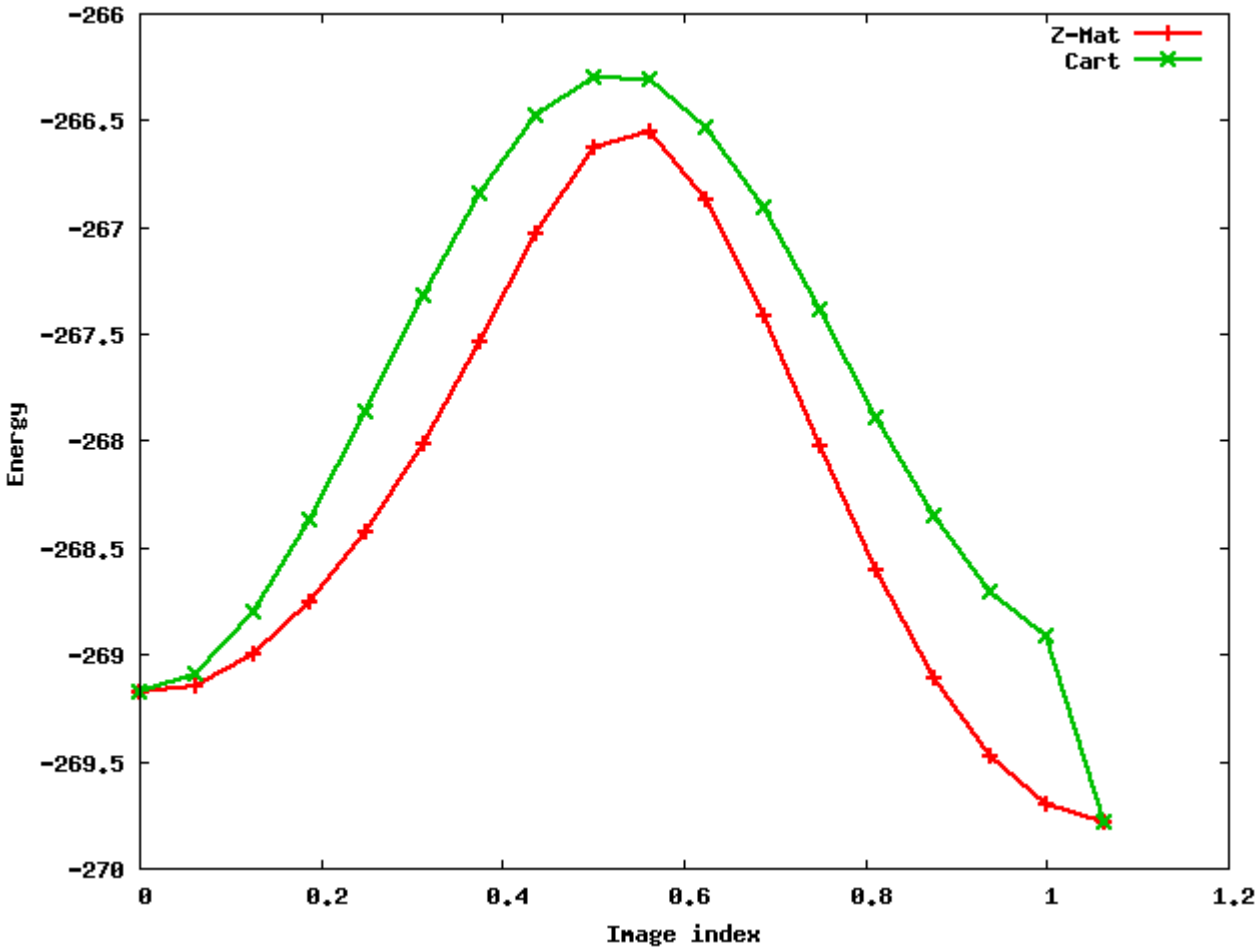


Zmat

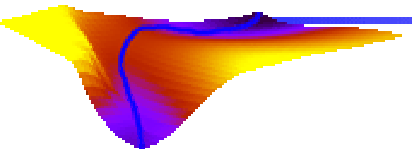
Catalytic hydrogenation



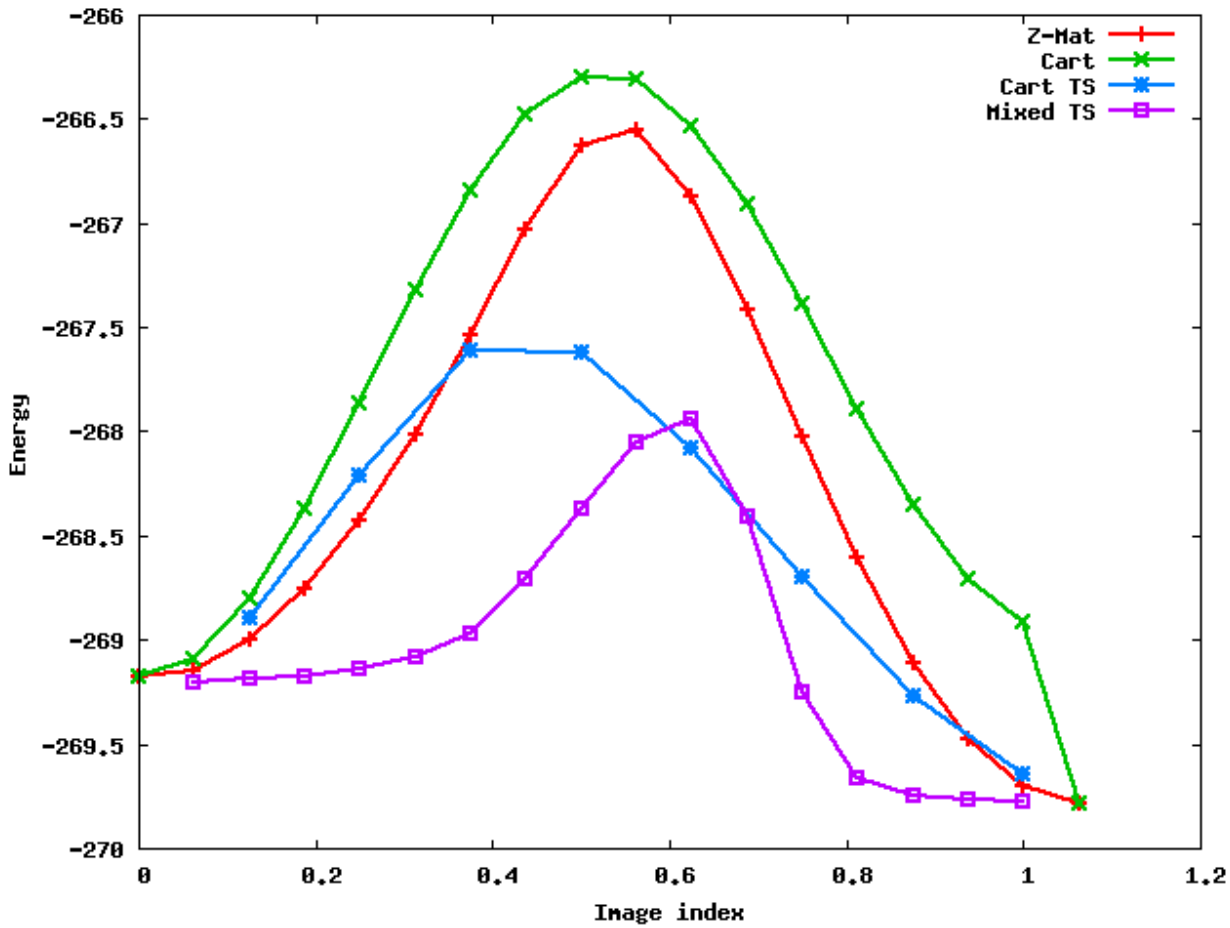
- Energies



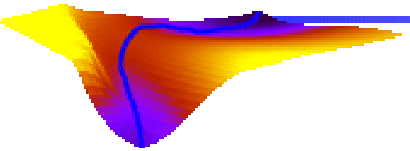
Catalytic hydrogenation



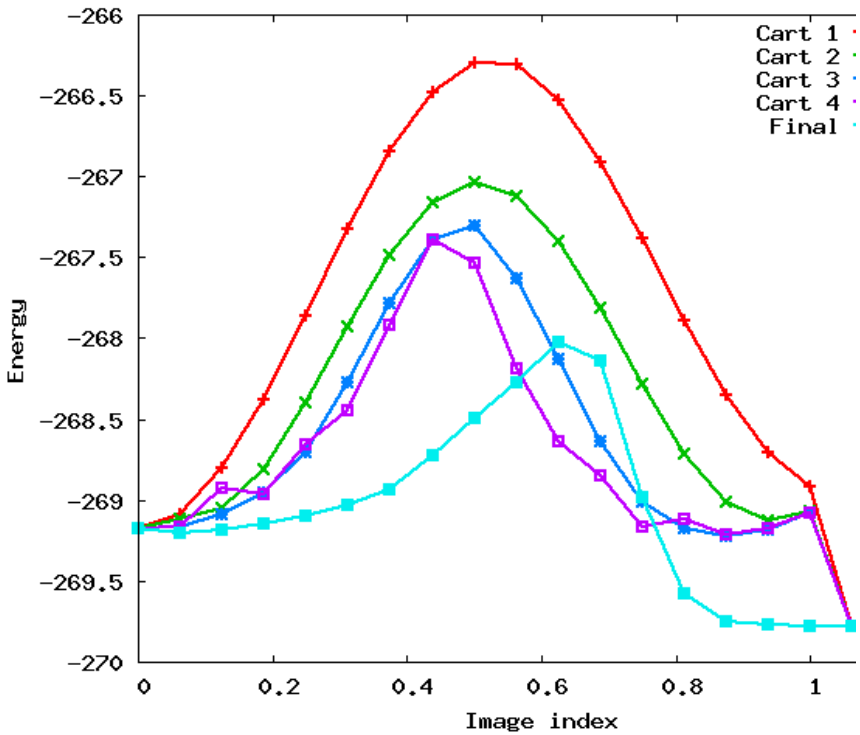
- We add some chemical intuition for the TS

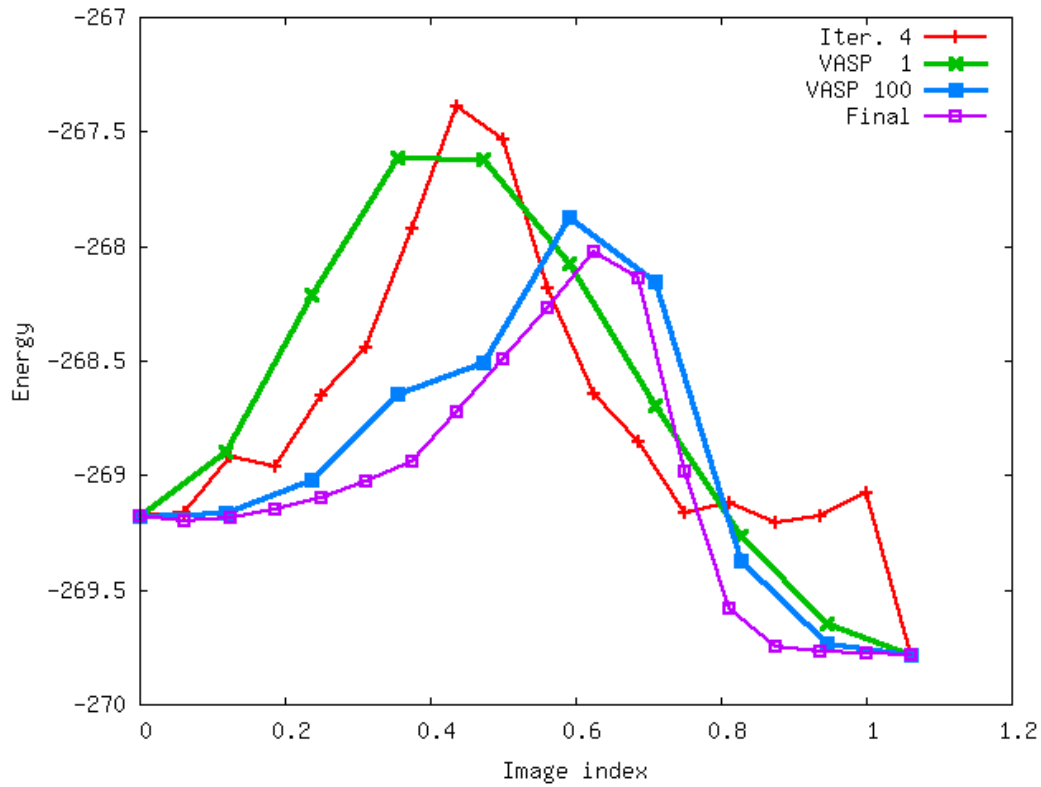


Catalytic hydrogenation

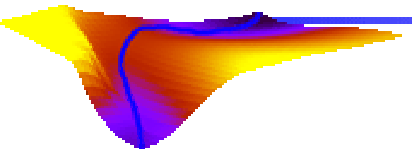


- Reading math book is not useless...





Conclusions



- On the PES (0K)
  - Mixing cart+Zmat for initial path
  - Good optimizer
  - Baker ?
- On the FES (300K)
  - Hopefully our procedure can help us choosing RCs
  - More to come...

Acknowledgements

- People
  - P. Dayal: Baker coordinates
  - J. Garrec, C. Dupont, F. Delbecq, D. Loffreda: beta testers.

- Money
  - ANR
  - Région Rhônes Alpes

ANR AGENCE NATIONALE DE LA RECHERCHE

CLUSTERS DE RECHERCHE RHÔNE-ALPES CHIMIE

... Thank you for your attention !